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# Movement of Atrazine in Soil Under Furrow Irrigation

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Dedicated to the Honored Memory

of

DR. STERLING A. TAYLOR

# MOVEMENT OF ATRAZINE IN SOIL

# UNDER FURROW IRRIGATION

by

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Jyothi Veerabhadrappa

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Movement of Atrazine in Soil

Under Furrow Irrigation

by

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Movement of atrazine in response to furrow irrigations was studied using the samples of Timpanogos silt loam soil. Distribution in soil profile of surface applied herbicide was determined by drawing samples of water extracts through porous cylinders. Atrazine quantity was determined by spectrophotometer.

It was observed that the herbicide found in the water extracts was an indication of the quantity present in the soil. The herbicide moved readily with the applied water. Irreversible thermodynamic model could not be applied because of the initial and final boundary conditions. The pattern of movement was in conformity with the chromatographic theory.

(66 pages)

# INTRODUCTION

## Extent of Herbicide Use

The number of herbicides manufactured and recommended for application to the soil increases every year. Application of herbicides has been practiced for hundreds of years (Brian, 1964). The important milestones in weed killing are the introduction of the first organic chemical, 2-methyl-4, 6-dinitrophenol (DNOC) in 1932 (Brian, 1964). A few years later, the important discovery was made that chemicals related structurally to plant hormones were selective in their effect on plants. New herbicides are now being produced at a high rate. Some of the popular herbicides now in use were unheard of a few years ago. With the large range of herbicides now available, it is possible to almost completely eliminate hand weeding.

A higher degree of weed control may be achieved with chemicals that are usually applied to the soil than with those that are applied to plant foliage (Klingman, 1961). There are differences between herbicides with respect to their persistence in the soil (Audus, 1964). Some herbicides may disappear completely from the soil within a week or two. Others may remain in toxic concentrations for a period of two or more years. The degree of persistence varies considerably with such soil conditions as texture, moisture content, temperature and organic matter (Klingman, 1961). It is well known that the inactivation of herbicides in soils is largely a reflection of the ease with which they are decomposed.

When an herbicide is applied to the soil, for the purpose of killing undesirable vegetation, some side effects may be expected. These effects may be directly influenced by one or more kinds of the micro-organisms that inhabit the soil. The disturbance of microbial populations might ultimately affect fertility adversely. Herbicides persisting for long periods in the soil might damage or reduce the yields of sensitive crops grown in subsequent seasons.

## Disappearance of Herbicides

Herbicides applied to the aerial parts of the plants may drip from the leaves to the soil surface. They may also reach the soil on the residue of the plants to which they were applied (Audus, 1964). Freed et al. (1962) listed the following factors that reduce the effectiveness of herbicides in the soil:

1. Adsorption on the surface of soil colloids.
2. Leaching from the soil thus reducing the concentration.
3. Volatalization into the atmosphere.
4. Microbial breakdown to simple harmless products.
5. Chemical breakdown to simple non-toxic products.
6. Removal by plants thus reducing concentration.

The movement of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) through the soil during simulated furrow irrigations is investigated in this study.

# REVIEW OF LITERATURE

Herbicide applied to the soil does not come in contact with the target organism until diffusion and water flow move the herbicide to the plant. This movement is in turn influenced by environment, weather, soil properties and the rate of application (concentration).

Transport of herbicides within the soil takes place as: diffusion through soil air, diffusion through soil water and flow with moving water (Hartley, 1964). It is characteristic of diffusion that any initial inequality spreads out in a spatial manner where measurements of distance across the affected zone are proportional to the square root of the time elapsed.

## Diffusion through Soil Air

The diffusion through soil air is of importance in the movement of volatile and gaseous substances. Diffusion coefficient, D, is defined by the equation

$$\frac{Q}{t} = D \cdot A \frac{-\partial c}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q is the rate of transfer, A is the cross sectional area normal to the direction x of diffusion, c is concentration and t is time.

The coefficient D so defined is not equal to that in uniform, unobstructed air because the actual pathways available for diffusion are tortuous and thus longer than the direct distance. They are also of non-uniform cross sectional area (Hartley, 1964). For this reason it is necessary to multiply the free diffusion coefficient by the

so-called tortuosity factor. This factor can be measured experimentally. Buckingham (1904) estimated the diffusion of carbon dioxide in soil to be equal to the porosity. Penman (1940) found a proportionality constant of about 0.6 for a variety of soils and for degrees of packings of glass beads. Call (1957) found the factor $\frac{D}{Do}$ to be approximately equal to:

$$\frac{D}{Do} = \frac{0.66(s-0.1)}{} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where s is the fraction of total volume occupied by water and air. D is actual diffusion and Do is free diffusion. This indicates that no diffusion occurs, if $s \leq 0.1$.

## Diffusion through Soil Water

Water soluble herbicides that are not volatile may diffuse through the soil water.

### Influence of water content

It is well established experimentally (Hartley, 1964) that the tortuosity factor does not vary greatly among different soils. It is approximately the same whether air or water is the diffusion medium, as long as the medium fills the spaces between the particles. This is because the geometry of the pathways does not differ whether the space is filled with air or water. In normal agricultural soils, however, water occupies only part of the volume between the particles, the rest being air filled. When the soil is at field capacity or drier, water is contained only in the finer cavities or at the points of contact of solids. The water is thus substantially less continuous than the air space.

Klute and Letey (1958) conducted a study of ionic diffusion of $Rb^{86}Cl$ through 200 μ glass beads at different moisture levels. The tortuosity factor fell from 0.45 at 33 percent moisture to 0.05 at 20 percent moisture content. Stewart and Eck (1958) studied the extent of movement of surface applied ammonium nitrate into Tillman clay loam soil that had been adjusted to each of five different moisture levels. The soil was incubated at constant temperature for 14 days and the nitrate determinations were made on samples taken from different depths. They found that nitrate had moved downward to the extent of 2.5 inches when the soil moisture was at field capacity and to 1.5 inches in all drier samples. At the water contents of 18.2 percent, 8.3 percent and 6.6 percent, about 14.8, 5.5 and 1.2 percent, respectively, of the originally applied nitrate was found below a depth of 1.5 inches. Porter et al. (1960) obtained a transmission index or tortuosity factor by dividing the diffusion coefficient of chloride obtained from the soil systems by the diffusion coefficient of chloride in pure water. They found a linear increase in the tortuosity factor with moisture content. In loam soil, the factor was zero at nine percent and increased to 0.32 at 28 percent soil water. For clay it was zero at 13 percent and increased to 0.28 at 44 percent soil water.

Normally, one could expect the tortuosity factor to increase with decreasing moisture content, i.e., the ions would have to follow a more tortous path.

The tortuosity factor thus obtained is dependent on moisture content and falls to zero at a finite moisture content. It has been

estimated by Hartley (1964) that molecules of the size of herbicides will have diffusion coefficients in free water of about $5 \times 10^{-6}$ $cm^2$ $sec^{-1}$. In soils at field capacity the diffusion coefficient only one-fifth as large or $10^{-7}$ $cm^2$ $sec^{-1}$.

Influence of soil texture

A fine textured soil has a higher moisture holding capacity, than a coarse textured soil. Hence, at a given moisture content there is difference in the continuity of water. Porter et al. (1960) observed by extrapolation that approximately 7, 10 and 15 percent water content brought about zero transmission for loam, silty loam and clay, respectively. They assumed that at these moisture levels, the continuity of water films was completely destroyed. The fact that the transmission factor extrapolates to zero at higher moisture contents for the finer textured soils indicates that the diffusion of a chemical through soil adsorbed water is very small.

## Role of Diffusion in Moving Herbicides into Soil

Most of the important herbicides are sufficiently nonvolatile (Hartley, 1961) that transfer through soil water seems to be more important than transfer through soil air. Diffusion through air may be ignored for all the herbicidal acids and for those having polar hydrophilic group (Hartley, 1961).

Under static conditions of moisture or where percolation rate is slow, diffusion may become important in distributing the chemicals through the soil profile. Logan et al. (1953) observed that radioactive isopropyl N-phenyl carbamate (IPC) was further redistributed

upon standing after the usual distribution resulting from leaching of soil columns.

Downward movement of surface applied nitrate in Tillam clay loam soil under certain moisture conditions in which liquid water was not moving, has been observed by Stewart and Eck (1958). The extent of downward movement was as much as two and a half inches when the soil was at the moisture equivalent. Similar trends were reported by Tyler et al. (1958) with dissolved solutes and by Del Pozo (1959) with trichloro-benzoic acid (TBA). Upchurch and Pierce (1957) have shown that when the rate of percolation of water is slow, there will be ample time for redistribution of dissolved chemicals through the diffusion process.

Diffusion of herbicides over long distances in soil has generally been considered to be negligible. Harris (1964) observed that dicamba and diphenamid moved downward with percolating water and upward when free evaporation was permitted from the surface. The upward movement almost ceased when the soil was covered to prevent evaporation. Lack of movement in the covered soil suggested that the herbicide was carried with the water moving to the evaporating site and diffusion was negligible. Hartley (1961) claculated that when sparingly soluble herbicide were applied on the surface, several years would be necessary for as little as one percent to migrate by diffusion to a depth of two feet in a moist soil. Diffusion is, however, an important means of transport of herbicide molecules over distances up to one mm from the surface of a soil (Hartley, 1964).

## Flow with Moving Water

Water moving downward or laterally through a non-absorbent porous medium might be expected to carry a soluble surface applied herbicide in amounts that are somewhat proportional to the total liquid flow. In soil many physio-chemical and biological phenomena are encountered that modify the extent of the movement that occurs.

Hill (1956) suggested that texture, structure, temperature, moisture content, organic content, chemical composition of the soil and the nature and extent of microbial population are soil factors that influence the proportionality between water flow and the herbicide contained in it. Other factors are herbicide formulation and solubility of herbicide.

### Influence of flow rate and direction

As a herbicide is carried through the soil profile by flowing water, it tends toward an equilibrium between the dissolved phase and the adsorbed phase. Herbicide molecules are continually being adsorbed and released by the surface of the soil particles.

Prior to applying water one might find a high concentration of soluble pesticide near the surface of the soil. The zone of highest concentration may move progressively downward as the maximum depth of wetting increases. The zone of highest concentration becomes more diffuse as the amount of movement increases. The distribution might resemble a normal probability curve with increasing standard deviation with increasing movement of herbicide. This type of wave movement has been observed by Sherburne *et al.* (1956), Freed (1958), Del Pozo (1959),

Phillips (1959) and Lambert et al. (1965). Some workers have suggested a mathematical formula for the concentration distribution in the profile at different times.

Based upon the results of experiments on two soils using radioactive labeled monuron, Sherburne et al. (1956) developed an equation to describe the depth for maximum concentration of the herbicide for the two soils at particular moisture contents and for a given amount of percolating water. They applied herbicide to the surface of soils which had been adjusted to predetermined moisture levels. Water was added in the amounts of one, three and nine inches. The labeled monuron was measured after 24 hours. Their equation is

$$y = xe^{-c/x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where: y = depth of the concentration peak after 24 hours (inches)

x = water applied initially at the soil surface (surface inches)

c = constant

e = base of natural logarithms

Freed (1958) suggested an equation to describe the depth of maximum concentration of herbicide as a function of the amount of applied water.

The equation is

$$y = x\, e^{\frac{-\Delta H}{RTX}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where: y = depth of maximum concentration (inches)

x = water applied (surface inches)

$\Delta H$ = enthalpy of adsorption (K. cal/mole)

T = temperature ($^{o}K$)

R = universal gas constant (cal/deg mole)

Lambert et al. (1965) derived a mathematical expression to describe the concentration of herbicide along the soil profile as follows:

$$C = \frac{Q}{\delta\sqrt{2\pi}} \exp - \left[ \frac{(x - x_o)^2}{2\delta^2} \right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In this equation:

c = concentration of the chemical at point x in the column (gm/cm of column length)

$\delta$ = spreading factor which measures the column efficiency (cm)

x = distance measured from the surface to the point under consideration (cm)

Q = quantity of chemical added to the column of soil (gm)

xo = distance measured from the top of the column to the point of maximum concentration of the chemical (cm)

Ogle and Warren (1954) made two types of herbicidal movement studies: (a) A percolation study designed to follow the movement through soil columns following the addition of 2 inches (5.1 cm) of water and (b) A leaching study designed to determine the relative amounts of infiltration required to remove completely the herbicides from the surfaces of three types of soils. They tried to relate the degree of leaching with the molecular size, solubility, and probable chemical reactions in the soil. The downward movement of herbicide from the soil surface did not follow what they considered to be consistent patterns when they irrigated with 16 inches (40.6 cm) of water.

Upchurch and Pierce (1957) found that 4 inches (10.02 cm) of water applied as simulated rainfall in eight increments at half hour intervals caused 72 percent of a 40 lb/A application of monuron to Lakeland sand to be leached below 2 inches (5 cm). Twelve inches (30 cm) of simulated rainfall applied in a similar manner caused 89 percent to

be leached below 24 inches (cm). Single applications of rainfall varying from 1/16 inch (.16 cm) to 4 inches (10.02 cm) had little influence upon the movement of monuron from the 0- to 2-inch (0 to 5 cm) soil layer, but applications less than 1/16 inch (.16 cm) resulted in a greater accumulation of monuron in the 2- to 8-inch (5 to 20.4 cm) zone than in any other layer. Frequent applications of simulated rainfall resulted in a greater accumulation of monuron in a shallow zone below the surface but greater removal from the surface layer than less frequent applications.

In the field studies made by Burnside et al. (1963) it was found that 38 inches (96 cm) of rain was not sufficient to remove all of the herbicide from the 3- to 24-inch (7.6 to 60 cm) soil depth.

The movement of surface applied herbicides under furrow irrigation will not be the same as that under overhead irrigation because the herbicide follows the streamlines. Haise (1948) demonstrated the water flow pattern under furrow irrigation using a soluble dye. Bernstein and Fireman (1957) revealed that concentrations of salts was higher along the locus of points at which the opposing wetting fronts meet than at points behind the wetting fronts. Ashton (1961) investigated the pattern of herbicide movement in a simulated furrow irrigation system. He used a box of soil 12 inches (30 cm) wide by 18 inches (45 cm) deep by 24 inches (60 cm) long. A furrow was made in the center of the 12 inch (30 cm) dimension. Urea and triazines were applied at the rate of 10 lbs. per acre on the soil surface in a band 1 inch (2.54 cm) wide and one-half inch (1.27 cm) away from the edge of the furrow. Water was added to the furrow by means of a

constant leveling device. The irrigation was stopped when the wetting front at the surface reached the outside edge of the soil. He observed a considerable lateral movement for all the herbicides and all the different soils that he used.

Apart from the movement of the herbicide in the water and diffusion, Day (1956) concluded that hydrodynamic dispersion brings about extensive dilution and spreading of dissolved solutes (we may consider herbicides as solutes).

Influence of solubility of herbicides

Solubility of herbicides has been considered by Hartley (1960) to control herbicide movement through the soil in irrigation water. The solubility of a chemical under conditions of equilibrium between the pure solid chemical and the dissolved phase is a function of temperature and latent heat of solubility as given by the equation (Freed et al., 1962)

$$\text{Log } s = \frac{\Delta H}{RT} + c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where: s = solubility at equilibrium

H - latent heat of solubility cal/mole

T = temperature ($^{o}K$)

R = universal gas constant cal/deg mole

c = log of solubility at reference temperature

The rate with which the chemical dissolves is a function of the state of dispersion. Thus, with the same mass of solid chemical, increasing the specific surface area by grinding the material will increase the rate of solution. This may, in turn, enhance the rate of

penetration into the soil. One inch of rain on an acre has the capacity to dissolve 1 lb of simazine which is one of the least soluble herbicides (5 ppm). The time required to dissolve spheres of 5 μ radius in an infinite body of stagnant water has been calculated by Hartley (1960) for some herbicides. Accordingly, trichloroacetic acid (TCA) takes only a few seconds, calcium salts of 2, 4-D take a few minutes, while monuron with solubility of 230 ppm needs 3/4 hour and simazine needs 30 hours.

Burnside et al. (1963) found that atrazine showed more leaching and greater loss from the 0- to 3-inch soil depth than simazine or monuron. A similar trend was observed by Ashton (1961).

When the herbicide is applied in granular form, the rate of solution may be very much slower. Hartley (1964) concluded that low water solubility retards the flow of herbicide into soil. He also concluded that the solubility of herbicides in the soil is apparently much higher than it is in the pure water.

Ogle and Warren (1954) were unable to predict movement on the basis of the solubilities and the molecular sizes. Trichloroacetic acid (TCA) leached from the soil surface readily and if any was retained after 2 inches (5.1 cm) of water had passed through the soil, it was biologically inactive. Monuron, however, was still present in the surface in a highly toxic concentration after passing 16 inches (40 cm) of water through a sandy soil. Since it is soluble up to 230 ppm, the amount of water applied should have dissolved 400 times the quantity of the herbicide originally applied. Therefore, they assumed that monuron was held by soil in an active form. Harris (1966)

observed that prometryne (solubility 48 ppm) offers more resistance to movement than simazine (solubility 5 ppm) and atrazine (solubility 70 ppm).

Influence of adsorption of pesticide

Frissel and Bolt (1962) observed that adsorption of herbicides is strongly dependent on conditions varying both in sign and magnitude of charge on clay minerals. In addition, pH and electrolyte concentration also affect the adsorption. They prepared a table listing the expected percentage adsorption and concentration in the soil solution for homogeneous distribution of the herbicides in a 20 cm furrow slice at about 20 percent moisture content.

Upchurch and Pierce (1958) examined the descent of surface applied monuron over the dosage range of 0.25-256 lb/acre. They found that there is no significant difference between the proportions of monuron found at various depths.

Frissel and Bolt (1962) opined that there is no especially strong attraction between herbicides and clays. The enormous surface area available can accommodate the herbicide molecules at a very low density. At the concentrations of practical interest, the clay fractions of soil would need to have only 0.001 or less of total clay surface covered by herbicide molecules in order to adsorb all that was present.

Generally, the forces producing adsorption represent a balance of the water-clay, clay-herbicide, and water-herbicide attractions.

The adsorption patterns are likely to be affected by the types of herbicides and by the soil texture, pH, and temperature. Lowering pH

resulted in increased adsorption by bentonite. The influence of pH was not the same on all the herbicides studied. There was no relation between water solubility and adsorption (Talbert and Fletchall, 1965; Harris and Warren, 1964). Adsorption of herbicides on bentonite at pH 8.5 was much greater at 0 C than at 50 C. But adsorption by muck was the same at either temperature. Desorption of herbicide was accomplished more readily from bentonite than from muck. They found that there was total adsorption of atrazine by the cation exchanger. They explain that as pH is lowered, more $H^+$ ions associate with the triazine molecules to give them more cationic characteristics which leads to more adsorption on the negatively charged clays. Lack of adsorption by muck at lower pH may be caused by the loss of exchange sites as a result of $H^+$ ions associating with carboxyl and hydroxyl groups. These groups offset the increased charge on the atrazine molecules.

Harris (1966) observed that ametryne was more strongly adsorbed than atrazine. The molecular structures of these two herbicides are similar except the $SCH_3$ group appears in ametryne in place of the Cl group in atrazine. This suggests that the $SCH_3$ group might influence the electron density of the molecule in such a way as to cause strong adsorption.

Using radioactive ametryne and atrazine, Yang (1966) observed that the adsorption of these herbicides was reciprocal proportional to the temperature; thus the heat of adsorption is positive. The amount of adsorption was shown to be depending upon the concentration in solutions also.

Hill (1956) recognized that organic matter content is one of the important factors in the movement of herbicides. Upchurch and Pierce (1958) changed the organic matter content in the soil by replacing soil at lower depths with that from deeper depths. Organic matter content ranged from 0.70 percent to 1.44 percent. The amount of monuron retained in the 0 to 8-inch (0 to 20 cm) layer varied from 35 to 95 percent depending upon the organic matter content which was in the range of 1.07 to 1.44 percent in those depths.

It promotes microbial activity, which in turn, breaks down the pesticides. Breakdown of 2,4-D by micro-organisms is reported by Hernandez and Warren (1950). Brown and Mitchell (1948) and Ogle and Warren (1954). Harris and Warren (1964) and Yang, M.S. (1966) observed that the adsorption decreased with increasing temperature. The reduced rate of adsorption thus allows more herbicide to become free to move.

The vicosity decreases with an increase in temperature and thus the hydraulic conductivity K increases.

The increased mobility of herbicides under increasing temperature has been observed by Upchurch and Pierce (1958), Freed (1958), and Freed et al. (1962).

Irreversible thermodynamic model

In thermodynamics it is assumed that when a system has been left isolated for a sufficient length of time, it will reach a state of dynamic equilibrium, where all the visible properties of the system remain constant. The approach to equilibrium is irreversible (Onsager, 1931).

The movement of water, heat, solutes, electricity and matter has been considered in terms of irreversible thermodynamics. The movement of one or more of these substances influence the flow of all others that are present.

In many instances, the flow of water in soil is influenced by forces other than those arising from a moisture content or water potential gradient (Taylor and Cary, 1960). They proposed the use of thermodynamics of irreversible processes and linear rate equations containing Onsager's reciprocal relations as a tool to analyze the simultaneous flow of water and salt, water and heat, or water and electricity in saturated and unsaturated soils (Taylor and Cary, 1964). They also confirmed the validity of Onsager's relationship in analyzing the simultaneous flows of heat and water.

Yang (1966) studied the simultaneous movement of triazines in unsaturated soils and adopted the irreversible thermodynamic model to describe their flow.

## Other Methods of Herbicide Dissipation in Soils

In addition to adsorption, leaching and run-off with water, herbicides are subject to other forces that tend to reduce their quantities or activities. Important of these are: (1) chemical breakdown, (2) microbial decomposition and (3) uptake by crops.

### Chemical breakdown

Soil applied herbicides that are in general use have been developed to leave a balance between stability and resistance. Highly unstable compounds are of little value for killing plants by soil application

and root uptake because they do not survive long enough to come into contact with the plant. On the other hand, compounds which are resistant to decay for periods much longer than one growing season may create problems to subsequent sensitive crops. Such compounds may be desired for long-time sterilization, but are of little value in selective weed control.

Slow hydrolisis is a common reaction. -C-Cl, -C-O-$CH_3$ and -C-S-$CH_3$ groupings of the triazines are subject to hydrolysis in sterile solution (Hartley, 1964). The reactions appear to progress with significant speed under either strongly acid or alkali conditions. Adsorption on soil colloids may either retard or more frequently accelerate chemical reaction. Simazine is generally reported to be less effective and less persistent in soils with a high organic matter content than in soils with less organic matter (Roadhouse and Birk, 1961). Increased hydrolysis of an absorbed chemical has been attributed to molecular distortion in the absorbed state. In addition, the extensive contact of adsorbed herbicide with atmospheric oxygen could lead to more rapid oxidation than would occur in nonadsorbed herbicide that had less surface exposed. Oxidation is more likely to be affected by adsorption than is hydrolysis.

Chemical decomposition of any kind decrease the herbicide present in the soil, hence it directly decreases the opportunity for the herbicide to be taken up in active form by the plants. Hartley (1964) concluded that if reactions can occur in adsorbed state and especially if adsorption accelerates decay, the fraction of the dose which is available for transfer will be reduced considerably.

Microbial decomposition

Hernandez and Warren (1950) observed strong correlations between the rate of soil applied herbicide disappearance and the extent to which the conditions of soil were favorable for bacterial growth. Disappearance of 2,4-D was favored by such soil conditions as warmth, high moisture and high organic matter content. Crafts and Drever (1960) have shown that decay occurs in an exponential manner with time after application.

After the introduction of chemical into soil, the initial decomposition is very slow as the strains of some microbiological species are becoming adapted to the new chemical. This initial phase may be adrupt or very gradual in soil as the herbicide moves from a heavily contaminated surface soil to almost completely herbicide free deeper soil.

Absorption by crops

Corn is quite insensitive to triazines. This has been shown to be a result of herbicide decomposition by a harmless mechanism within the plant. Corn, in fact, takes up simazine at least as readily as do much more sensitive plants (Montgomery and Freed, 1961). Most of it is converted into simpler and harmless substances by the action of enzymes in the plant. Similar mechanisms may operate in other cases. The crop itself may thus be an important factor in total removal of the herbicide from the soil. Burnside et al. (1961) have domonstrated considerable removal of herbicides by the crop.

Some herbicide may be retained in the soil through the weeds which eventually succumb to the chemical. The dead parts of the

weeds fall onto the soil bringing the chemical back into soil. The portion of herbicide going through this cycle will be absorbed at certain soil depth by the roots. The deposition on the surface will initiate the movement of herbicide into soil all over again. Such biological activity will delay deep percolation and removal of the herbicide.

## MATERIALS AND METHODS

### Soils Used

These investigations were carried out using Timpanogos silt loam soils from the University Farms. The soil was collected from the 0 to 6-inch layer at random spots in the field. The soil was thoroughly mixed and air dried after removing the rocks and pebbles. The soil was then crushed to break the clods and passed through a 2 mm sieve.

### Containers

Boxes 12 inches (30 cm) long by 12 inches (30 cm) wide by 18 inches (45 cm) deep made of plywood were used for holding the soil. The sides were lined with a polyethylene sheet but the bottom was perforated to allow drainage. A half inch layer of gravel was spread on the bottom of each then Timpanagos silt loam soil was added until the boxes were filled to within 2 inches of the top. A furrow 1.5 inches (3.8 cm) wide and 1 inch (2.54 cm) deep was made to pass through the center of the soil in each box. This resulted in a furrow that was 12 inches (30 cm) long with 6 inches (15 cm) soil on either side.

Tensiometers were introduced at one corner of each box such that the porous cups were all at a depth of 12 inches (30 cm) from the surface. The tensiometers were used to observe the moisture tension. A drop in their readings was the signal to stop the irrigation.

All four boxes were kept in the greenhouse throughout the experimental period.

## Crop

The seeds of the corn, variety N.K. 199 Iachief, were planted in two rows at a distance of 2.5 inches on either side of the furrow. Thus, the distance between the crop rows was 5 inches (12.7 cm). After emergence, the plants were thinned to a spacing of 4 inches (10.2 cm) in each row, so that spacing between plants was 5 inches (12.7 cm) by 4 inches (10.2 cm). Three boxes were planted in this manner and the fourth was left unvegetated as a control. The crop was harvested after the third irrigation.

## Irrigation

A constant leveling device as shown in figure 1 was used for applying water to the soil through the furrow. The depth of water in the furrow at the time of irrigation was maintained at three-fourths the depth of the furrow. The device could maintain the water level in the furrow with a variation of 2 mm. One irrigation, sufficient to cause a drop in the tensiometer reading was applied at the time of planting the corn seeds. The soil required 2.5 surface inches (6.35 surface cm) of water to cause a drop in the tensiometer reading.

Subsequent irrigations were given on the basis of the moisture potential indicated by a tensiometer reading of 450 mm Hg (-59 joules/kg).

The first irrigation was called for and given to the boxes containing corn fifteen days after the application of herbicide. The second irrigation was required 15 days after the first and the last irrigation was called for just nine days after the second irrigation.

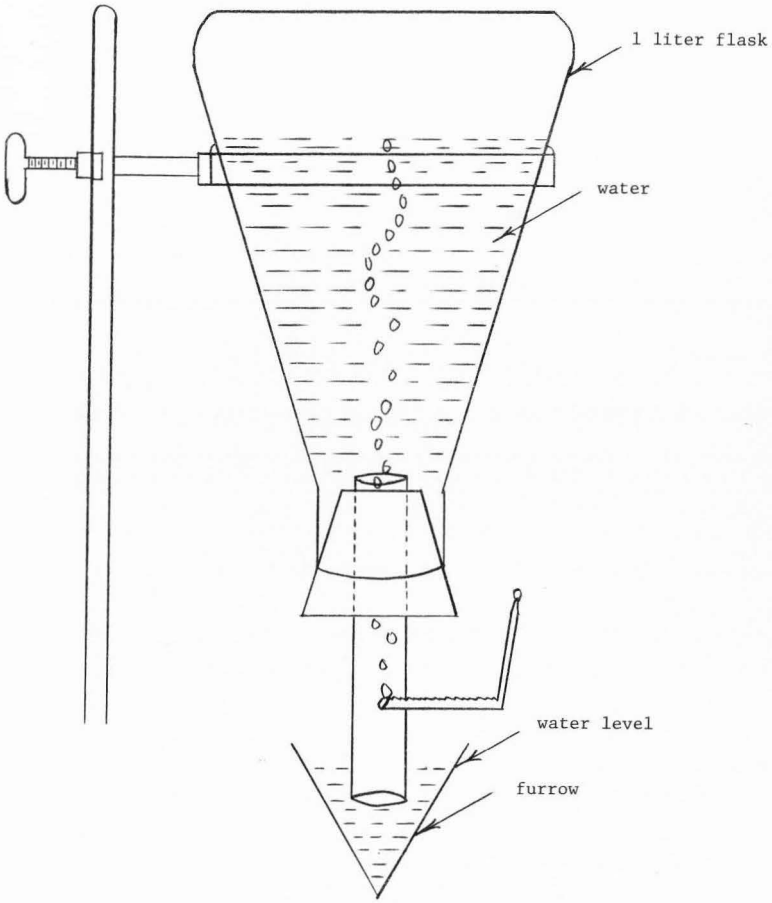


Figure 1. Constant leveling device.

The box without corn needed irrigation after every fifteen days.

## Herbicide Application

Two days after planting the corn seeds, a preemergence application of atrazine was made at the rate of 4 lb of active ingradient per acre in 100 gallons of water. Commercial atrazine containing 80 percent active ingredient supplied by Geigy Chemical Company was used. To apply 4 lbs per acre of active ingradient therefore 5 pounds per acre of commercial formulation was required. When reduced to quantity per box, this was 52.1 mg of commercial formulation in 9 ml of water. Thus 208.4 mg of atrazine were mixed in 36 ml of water and applied uniformly to the four boxes by using a small sprayer with a single fine nozzle. The nozzle was connected to constant air pressure for steady flow of spray. The herbicide was applied on the surface and was not incorporated into the soil.

## Sample Extractors

Filter cylinders (porous ceramic cups) 10 mm diameter and 55 mm high with 25 mm glazed top (Coors catalog number 762 with porosity P - ½AC) were used to extract soil solution. A long glass capillary was glued to the glazed portion of the cup with epoxy such that the seal was air tight. The other end of the capillary was bent at right angles twice to give the shape of an inverted "U." The tip of the tube after bending was 16 inches from the top of the porous cup. The end was fixed firmly in a number eight rubber stopper and inserted in a 2½ dram evacuated plastic vial containing a 9 ml glass vial in which

the solution was caught inside (see figure 2). A measured suction of 200 mm Hg (-26.2 joules/kg) was used to extract about 5 ml of soil solution.

The depths were measured from the surface of soil to the bottom of the porous cups, consequently the solution was actually drawn from a 30 mm space immediately above the specified depth. Samples were drawn from three different depths in each box.

Samples of soil solution were taken from the surface of the soil after the third irrigation. For taking these samples the cups were placed horizontally and parallel to the furrow (figure 3).

## Collecting Samples of Soil Solution

Prior to the application of herbicide, and following the first two irrigations after the application of herbicide samples were extracted from the depths of 2, 4, 8 and 12 inches (5.1, 10.2, 20.4 and 30 cm) from the surface. Surface soil solutions were collected only after the last irrigation in addition to the usual depths. This was done in order not to remove the herbicide from the surface in the early stages and to detect the extent of herbicide retention at the surface following treatment.

One hour after stopping the irrigation, a set of three extractors was introduced with the cups at a depth of 2 inches (5.1 cm). The cups were spaced 2.5 inches (6.35 cm) apart. One was at the center of the furrow, the second was at the crop row and the third at 2.5 inches (6.35 cm) outside the row. After collecting sufficient soil solution, the extractors were removed and a new set of three cups

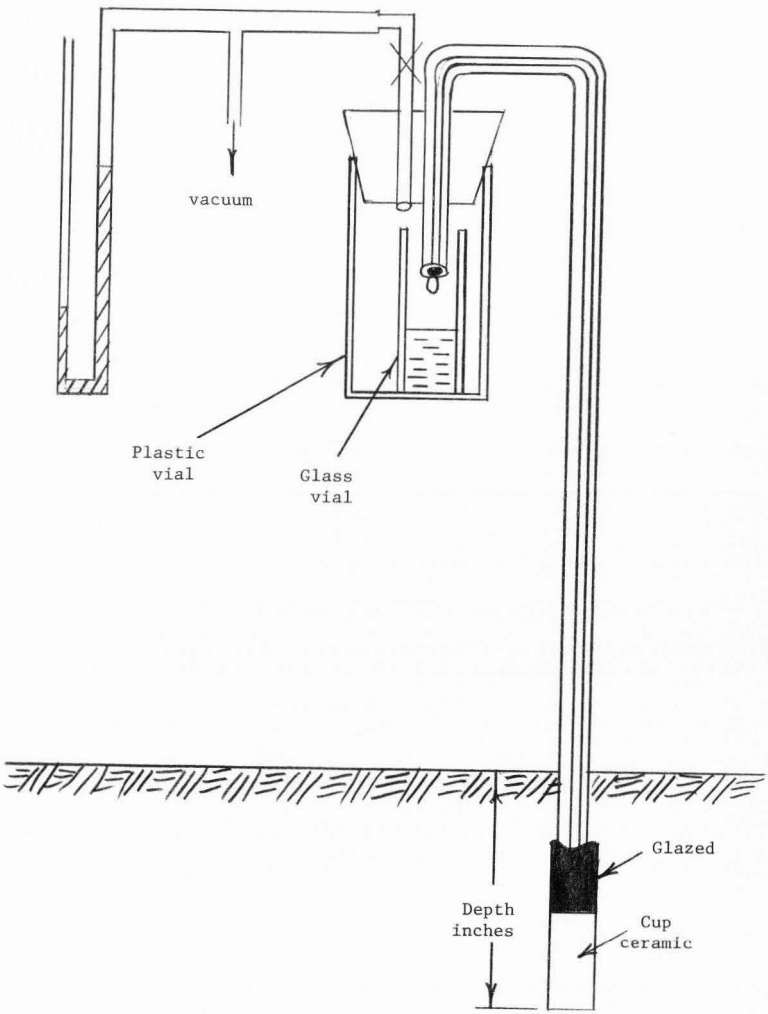


Figure 2. Sampling system.

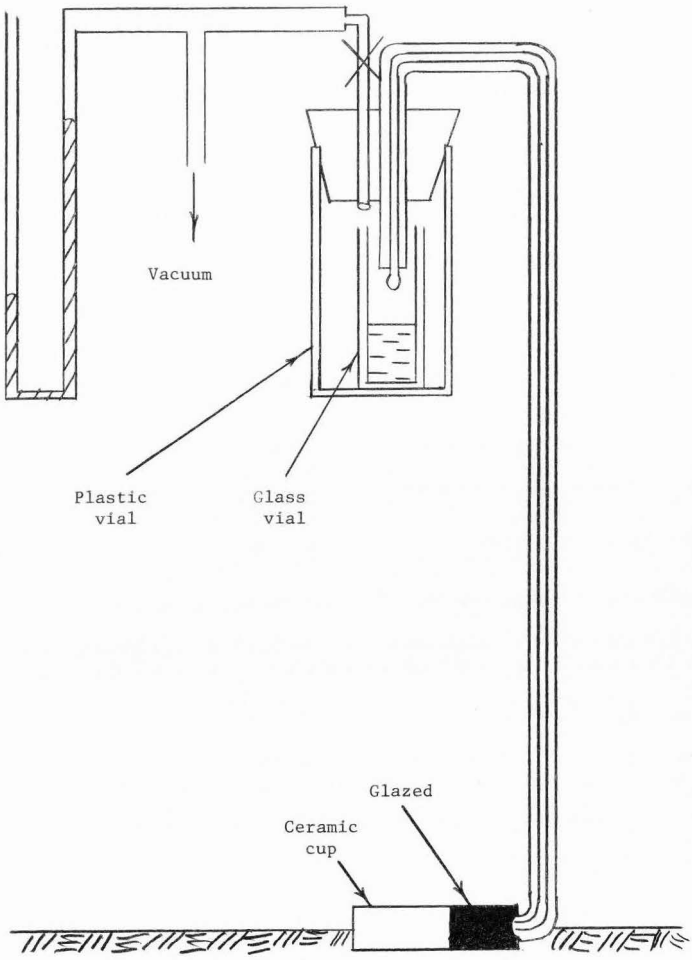


Figure 3. Surface sampling system.

introduced at the next depth. It took about 6 hours to extract each set of three samples at any one depth.

The L shaped extractors were placed on the surface at a distance of 1.75 inches (4.45 cm) and 3.50 inches (8.9 cm) from the furrow. They were thus at a distance of 1.25 inches (3.18 cm) on either side of the corn row. The horizontal extractor cups were pressed 0.5 cm into the soil surface (halfway through their girth).

All the water samples were stored in a dark cold room until they were used for analysis.

After each use, the cups were thoroughly washed with water. They were then washed with chloroform to remove all dirt and contamination.

The clean cups were immersed in a concentrated solution of atrazine and washed as described above before they were used for drawing soil solutions. This was done in order not to lose any herbicide from the soil solution through irreversible adsorption to porous walls of the cups.

## Soil Sampling

Soil samples were collected in a soil sampling tube that was 1 inch (2.54 cm) in diameter and 15 inches (38 cm) long. The samples were collected 12 days after the last irrigation since it was difficult to get undisturbed samples from the wet soil. The soil column in the sampling tube was sectioned into 0 to 2, 2 to 4, 4 to 8, and 8 to 12 inch (0 to 5.1, 5.1 to 10.2, 10.2 to 20.4 and 20.4 to 30 cm) portions. Each section was placed in a separate polyethylene bag, mixed thoroughly and stored in a dark cold room until analysis.

Sampling locations were: beneath the furrow and at 2.5 inches (6.35 cm) and 5 inches (12.7 cm) from the center of the furrow.

## Analysis

The soil extracts and the soil samples were analyzed by the methods outlined in "Analytic bulletin number 7" by Geigy Agricultural Chemicals Division. Atrazine is dissolved in carbon tetrachloride and passed through an aluminum oxide column to remove interfering materials. The chlorotriazine is converted to hydroxy triazine by acid treatment and subjected to spectroscoping observation. The hydroxy triazines have an absorption peak between 225 and 255 mμ with maximum at 240 mμ.

Standard solutions ranging from zero to 50 ppm were used to check the accuracy of the method.

One milliliter of solution was extracted twice with 5 ml portions of chloroform in a separatory funnel. The extract was then dried in the presence of anhydrous sodium sulfate on a steam bath then redissolved in carbon tetrachloride.

An absorption column was made from a glass tube 1 cm diameter and 60 cm long. One end was drawn into a narrow opening and a plug of glass wool was inserted to prevent loss of alumina. The tube was filled with 15 grams of activity V aluminum oxide and tapped gently to eliminate channeling of the alumina. Activity V aluminum oxide was prepared by thoroughly mixing 85 gm of basic alumina activity I with 15 ml of water and allowing to stand overnight in a tightly closed bottle before use.

The solution containing the dissolved extract residue in carbon tetrachloride was transferred to the column and allowed to penetrate

into the alumina. The container was washed twice with 5 ml portions of carbon tetrachloride which was also transferred to the column and allowed to penetrate as before. When all solvent had penetrated into the column, an additional 25 ml of carbon tetrachloride was added and allowed to percolate through the column. When the 25 ml of solvent had drained through the column, a clean 250 ml flask was placed as a receiver and 30 ml of five percent ethyl ether in carbon tetrachloride was added to the column and the elution continued. The whole 30 ml of eluent solution was collected for determining the atrazine.

The ethyl ether-carbon tetrachloride eluate was heated on a steam bath to remove the ethyl ether. It was then transferred quantitatively to a 125 ml separatory funnel. One ml of 1:1 (50 percent) sulfuric acid was added to the funnel. The funnel was shaken vigorously. The shaking was repeated every 15 minutes for 2 hours in order to convert the chlorotriazine to hydroxy triazine. Then 9 ml of water was added and the solution shaken. Upon separation of the layers, the carbon tetrachloride was drawn off and washed with 25 ml of ethyl ether. The aqueous layer was transferred to a 1 cm silica cell.

The absorbancy of the aqueous solution was measured in the 1 cm silica cell at 225, 240 and 255 mμ against a reagent blank on Hitachi Perkin-Elmer model 139 UV-Vis spectrophotometer. The net absorbance (E) was then determined at 240 mμ using a baseline technique according to the equation:

$$E = A^{240} - \left| \frac{A^{225} + A^{255}}{2} \right| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Here A is absorbance at specified wave lengths.

The baseline technique compensates for absorbance by interfering materials. The E valves so obtained represent absorbance by hydroxy triazines.

The soil samples needed additional pretreatments to extract the herbicides from the soil.

The soil samples were oven dried and homogenized by thoroughly mixing in a mortar and pestle. A 1 gm aliquot of soil was transferred into a 100 ml volumetric flask containing 10 ml acetonitrile. The mixture was refluxed for one hour in order to be cooled and filtered under vacuum through medium fritted glass filter funnel. The volumetric flask was washed and the washings added to the filtrate. The filtrate was then evaporated to dryness. From there on the procedure followed was the same as the one used for soil extracts.

## Design of Experiment

The investigations were planned for a randomized block design with three replications. Each box planted with corn was taken for a replication. The treatments were arranged in a three factor factorial design with irrigations sampling distances from the center of the furrow and sampling depths were the three factors. Irrigations and distances were each at three levels and the depths at four levels. Total number of treatments per replication was thus 36, with the total for the three replications being 108. The fourth box which was left without any vegetation has not been included in the statistical analyses, but was used to give a rough comparison with the treatments.

## RESULTS

### Results of Standard Solutions

Standard solutions ranging from 0 to 50 ppm concentration of active herbicide gave results that gave a straight line throughout. Absorbance readings of these solutions are given in Table 1.

Table 1. Net absorbance of dilute atrazine solutions as observed under spectrophotometer at 240 mμ.

| Concentration | Net absorbance |
|---|---|
| ppm | (E) |
| 0 | 0 |
| 5 | 22.5 |
| 10 | 38.0 |
| 15 | 60.0 |
| 20 | 82.0 |
| 30 | 118.0 |
| 40 | 152.0 |
| 50 | 200.0 |

The calibration curve of the standard solutions is represented in figure 4. This curve was used to convert the absorbance readings of the soil solutions to concentration of atrazine.

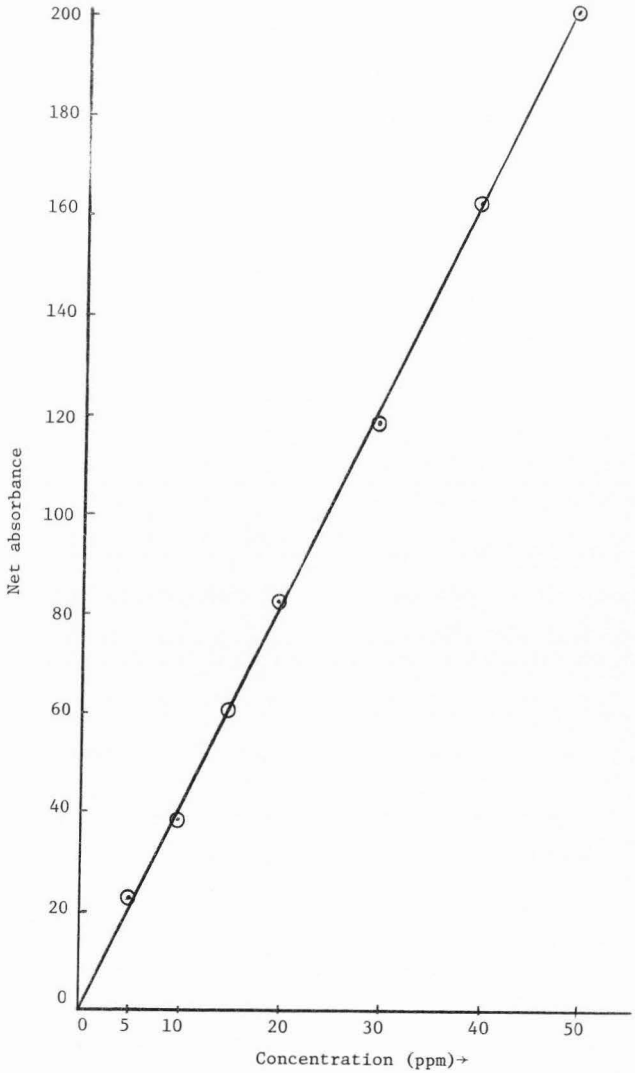


Figure 4. Absorbance at 240 mμ by std. solutions of atrazine.

## Quantity of Atrazine in Soil Extracts

The highest quantity of extractable atrazine found in the soil solutions did not exceed 20.5 ppm, although the solubility of atrazine is 70 ppm. There were, however, significant differences in the concentrations among the samples. The differences at different distances and depths were distinct. It is therefore assumed that the measured concentration of atrazine in the soil solution is a definite measure of the quantity present in the soil at the time and place of sampling. After each irrigation there was more soil leaching and outflow of solution from the boxes. Consequently, an unknown amount of atrazine that was in solution might have been lost from the system. The quantity of extract needed for chemical analysis was 1 ml. In order to get this, it was desired to collect 5 ml from each spot. This could not be accurately controlled, however, and sometimes the quantity collected was 8 or 9 ml.

The concentration of herbicide in the soil solution extract at different distances from the furrow and different depths from the surface for each of the three irrigations averaged over three replications and are given in table 2. The detailed data for each replication and treatment combination, including the control, are given in the Appendix.

The interaction of irrigation with distance in moving the herbicide are shown in table 3. The concentration in ppm of atrazine are averaged over the depths and the replications in this table.

The interaction of distance with depth was not significant and hence the table of interaction of these factors is deleted. The

Table 2. Concentration of atrazine in ppm found in soil solution drawn at three distances from the furrow and four depths from the surface.

| Irrigations | Depths | Distances from furrow in inches | | | | |
|---|---|---|---|---|---|---|
| | | 0 | 1.25 (3.18 cm) | 2.5 (6.35 cm) | 3.75 (9.5 cm) | 5.0 (12.7 cm) |
| | inches | ppm | ppm | ppm | ppm | ppm |
| 1 | 2 | 7.5 | | 5.75 | | 5.25 |
| | 4 | 4.16 | | 11.50 | | 9.75 |
| | 8 | 6.66 | | 8.58 | | 8.08 |
| | 12 | 3.25 | | 6.08 | | 7.00 |
| 2 | 2 | 2.25 | | 5.83 | | 6.08 |
| | 4 | 9.16 | | 7.50 | | 5.00 |
| | 8 | 5.66 | | 8.00 | | 6.58 |
| | 12 | 10.66 | | 9.42 | | 8.08 |
| 3 | Surface | | 10.58 | | 9.92 | |
| | 2 | 9.75 | | 9.58 | | 5.75 |
| | 4 | 9.25 | | 9.50 | | 6.33 |
| | 8 | 8.66 | | 9.58 | | 6.58 |
| | 12 | 9.00 | | 8.91 | | 6.33 |

Table 3. The interaction of irrigation with distance in the movement of atrazine in the soil. Data show the ppm of atrazine averaged over depths and replications

| Irrigations | Distance from furrow in inches | | | |
|---|---|---|---|---|
| | 0 | 2.5 (6.35 cm) | 5.0 (12.7 cm) | mean |
| | ppm | ppm | ppm | ppm |
| 1 | 5.39 | 7.98 | 7.52 | 6.97 |
| 2 | 6.93 | 7.68 | 6.43 | 7.02 |
| 3 | 9.16 | 9.39 | 6.25 | 8.27 |
| Mean | 7.17 | 8.35 | 6.74 | |

remaining first order (two factor) interaction that is irrigation with soil depth is given in table 4.

Atrazine content found in the surface soil solution after the third irrigation are given in table 5. The samples were taken at 1.25 inches (3.18 cm) on either side of the crop row. Statistical tests have not been conducted on these data.

## Quantity of Atrazine in Soil Samples

The soil samples taken at the distances of 0, 2.5 and 5 inches (0, 6.35 and 12.7 cm) from the furrow were sectioned into 0 to 2, 2 to 4, 4 to 8, and 8 to 12 inch (0 to 5.1, 5.1 to 10.2, 10.2 to 20.4, and 20.4 to 30 cm) portions. The samples from each section were analyzed for atrazine content. The detailed results of these analyses are given in table 6. The interactions of distances and depths averaged over replications are given in table 7.

Table 4. The interaction of irrigation with soil depth in the movement of atrazine in soil. Data show ppm of atrazine averaged over distances and replications.

| | | Irrigations | | | |
|---|---|---|---|---|---|
| Depth | | 1 | 2 | 3 | Mean |
| inches | cm | ppm | ppm | ppm | ppm |
| 2 | 5.1 | 6.07 | 4.72 | 8.36 | 6.42 |
| 4 | 10.2 | 8.47 | 7.22 | 8.36 | 8.39 |
| 8 | 20.4 | 7.77 | 6.75 | 8.28 | 7.60 |
| 12 | 30.0 | 5.44 | 9.39 | 8.08 | 7.64 |
| Mean | | 6.97 | 7.02 | 8.27 | |

Table 5. Atrazine content in ppm found in the surface soil solution at 1.25 and 3.75 inches from the furrow.

| Distance from furrow | | Replication | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Mean | Control |
| inches | cm | ppm | ppm | ppm | ppm | ppm |
| 1.25 | 3.18 | 11.00 | 9.50 | 11.25 | 10.58 | 10.50 |
| 3.75 | 9.50 | 10.00 | 9.25 | 10.50 | 9.92 | 13.25 |

Table 6. Atrazine content in ppm in the soil samples at 3 distances and 4 depths after the third irrigation.

| Distance from furrow | | Depth | | Replication | | | Mean | Control |
|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | 3 | | |
| inches | cm | inches | cm | ppm | ppm | ppm | ppm | ppm |
| 0 | 0 | 0 - 2 | 0.0-5.1 | 6.50 | 9.25 | 11.75 | 9.17 | 4.75 |
| | | 2 - 4 | 5.1-10.2 | 10.00 | 8.00 | 6.75 | 8.25 | 9.00 |
| | | 4 - 8 | 10.2-20.4 | 10.50 | 11.25 | 10.50 | 10.75 | 13.00 |
| | | 8 - 12 | 20.4-30.0 | 8.00 | 10.00 | 7.75 | 8.58 | 5.00 |
| 2.5 | 6.35 | 0 - 2 | 0.0-5.1 | 9.25 | 9.50 | 8.50 | 9.08 | 9.75 |
| | | 2 - 4 | 5.1-10.2 | 11.25 | 10.50 | 9.75 | 10.50 | 13.00 |
| | | 4 - 8 | 10.2-20.4 | 7.50 | 4.00 | 5.50 | 5.60 | 5.25 |
| | | 8 - 12 | 20.1-30.0 | 8.75 | 6.25 | 6.25 | 7.08 | 8.00 |
| 5.0 | 12.7 | 0 - 2 | 0.0-5.1 | 12.25 | 10.50 | 10.75 | 11.16 | 14.00 |
| | | 2 - 4 | 5.1-10.2 | 8.25 | 4.00 | 5.25 | 5.80 | 5.75 |
| | | 4 - 8 | 10.2-20.4 | 6.00 | 6.75 | 6.25 | 6.33 | 11.00 |
| | | 8 - 12 | 20.4-30.0 | 10.00 | 10.75 | 10.00 | 10.25 | 11.75 |

Table 7. The interaction of distance with depth in the movement of atrazines as observed in the actual soil samples. The tabulated values were averaged over replications.

| Depth | | Distances from furrow in inches | | | |
|---|---|---|---|---|---|
| | | 0 | 2.5 (6.35 cm) | 5 (12.7 cm) | Mean |
| inches | cm | ppm | ppm | ppm | ppm |
| 0 - 2 | 0.0 - 5.1 | 9.16 | 9.08 | 11.16 | 9.81 |
| 2 - 4 | 5.1 - 10.2 | 8.25 | 10.50 | 5.83 | 8.19 |
| 4 - 8 | 10.2 - 20.4 | 10.75 | 5.66 | 6.33 | 7.58 |
| 8 - 12 | 20.4 - 30.0 | 8.58 | 7.08 | 10.25 | 8.64 |
| Mean | | 9.18 | 8.08 | 8.40 | |

## Analysis of Variance

### Soil extracts

Statistical analyses were conducted on the results obtained from the soil extracts. These procedures did not include the results of control box and those of surface soil solutions. The details of the analyses are tabulated in table 8.

### Soil samples

Herbicide quantities found in the actual soil samples were put to statistical tests. The results of these tests are shown in table 9.

Table 8. Analysis of variance of soil extracts for all treatment combinations.

| Source | df. | S.S. | M.S. | F. |
|---|---|---|---|---|
| Replication | 2 | 9.22 | 4.61 | |
| Treatments | 35 | 466.53 | 13.32 | 3.56** |
| Irrigations (A) | 2 | 39.24 | 19.62 | 5.24** |
| Distances (B) | 2 | 50.57 | 25.28 | 6.76** |
| Depths (C) | 3 | 39.04 | 13.01 | 3.47** |
| A x B | 4 | 78.35 | 19.58 | 5.23** |
| A x C | 6 | 113.46 | 18.91 | 5.05** |
| B x C | 6 | 10.09 | 1.68 | 1 |
| A x B x C | 12 | 135.78 | 11.31 | 3.024* |
| Error | 70 | 261.61 | 3.74 | |
| Total | 107 | 737.36 | | |

*Significant at 5 percent level of probability.

**Significant at 1 percent level of probability.

Table 9. Analysis of variance of atrazine content in the soil samples.

| Source | df. | S.S. | M.S. | F |
|---|---|---|---|---|
| Replications | 2 | 4.02 | 2.01 | |
| Treatments | 11 | 125.68 | 11.42 | 4.91** |
| Distances (A) | 2 | 7.77 | 3.88 | 2.01 |
| Depths (B) | 3 | 23.80 | 7.93 | 4.10* |
| A x B | 6 | 94.11 | 15.68 | 8.12** |
| Error | 22 | 42.56 | 1.93 | |
| Total | 35 | 172.26 | | |

*Significant at 5 percent level of probability.

**Significant at 1 percent level of probability.

## DISCUSSION

Herbicides applied on the soil surface move mainly with the water. The water movement away from the furrow is both lateral and vertical. This is especially true near the surface. Haise (1948) has indicated that solutes will be leached away from the furrow and be deposited in the soil profile in somewhat of a radial fashion. He showed that solutes would be accumulated in the ridges between the furrows. After the soil becomes saturated, the movement will be vertically downward. When there is only one furrow for irrigation, the water flow lines will be nearly radial until the saturation point is reached, then they will be vertically down. When the soil begins to dry from the surface, the water moves up vertically. All these movements of water affect the distribution of surface applied pesticides in the soil profile.

### Effect of Irrigation on Downward Movement of Atrazine

Since some of the water movement directly under the furrow is mostly downward it can be expected that herbicide will move downward. According to the chromatographic theory suggested by Martin and Synge (1941), Wilson (1940) and Lambert *et al.* (1965), it can also be expected that herbicide will accumulate at certain depth according to the quantity of water flowing.

Profiles of concentration of herbicide below the furrow plotted in figure 1 for each irrigation appear to agree with the chromatographic theory. After the first irrigation, the herbicide appears to

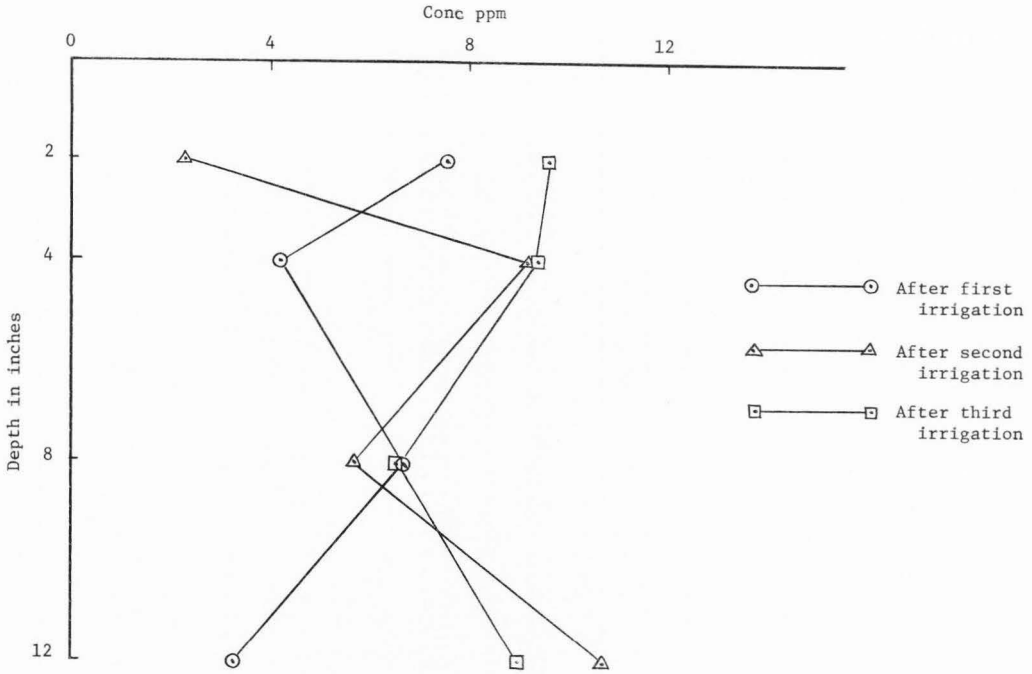


Figure 5. Quantity of atrazine in ppm found in soil solution at 4 depths at the furrow after each irrigation.

be concentrated at depths of 2 and 8 inches (5.1 cm and 20.4 cm). After the second irrigation, the concentration appears to be at 4 and 12 inches (10.2 and 30 cm). While no clear demarkation can be made after the third irrigation. The two concentration peaks observed after the first and second irrigations could be due to the upward movement of herbicide with the mass moisture flow and accumulation at certain shallow depth and at the surface. When irrigated, these two concentrated bands--one from the surface and the other from a shallow depth--moved down giving two heaves.

During the third irrigation, there seemed to be a uniform distribution along the profile due to diffusion, water movement and plant uptake of herbicide.

## Effect of Irrigation on Lateral Movement of Herbicide

Although the water applied at the furrow may distribute laterally and vertically, the surface applied herbicide may not move in the same fashion. At some distance away from the furrow, i.e., at 2.5 and 5 inches (6.35 and 12.70 cm) the movement has assumed a different pattern. The concentration profiles at 2.5 and 5 inches (6.35 and 12.70 cm) distance from the furrow are plotted in figures 6 and 7 respectively.

There is a significant effect of irrigation on lateral movement. After the first irrigation there seems to be an accumulation of herbicide at the 4-inch (10.2 cm) depth at both of these distances. After the second and third irrigation the accumulation seems to have been removed. The accumulation at the 4-inch (10.2 cm) depth could be partly due to the lateral flow of water while irrigating and partly

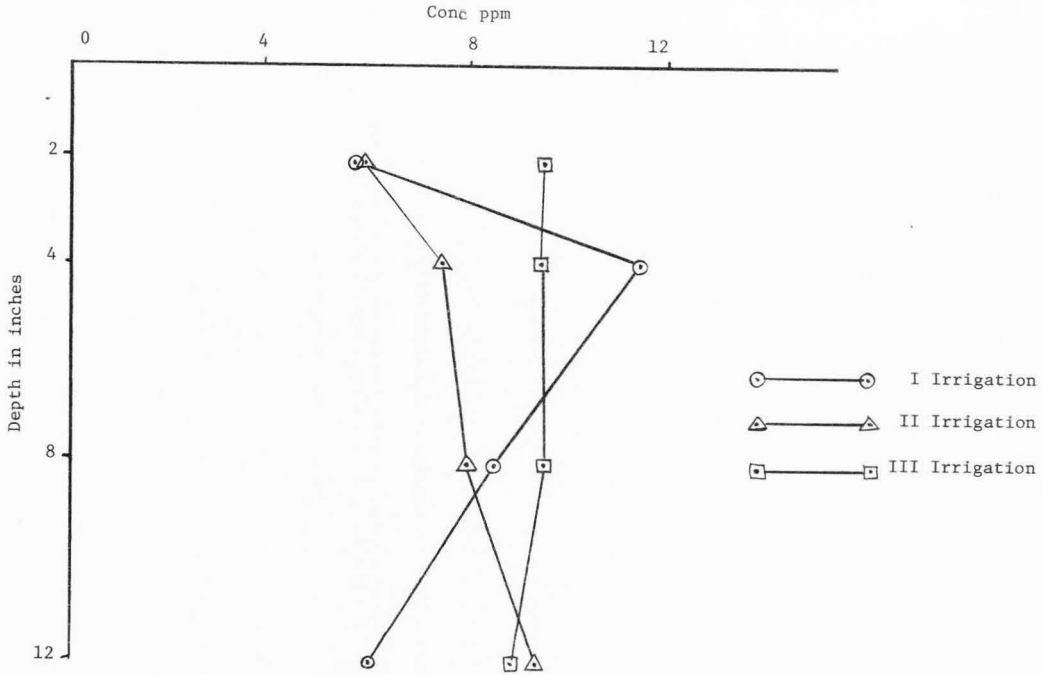


Figure 6. Quantity of atrazine in ppm found in soil solution of 4 depths at a distance of 2.5 inches from the furrow after each irrigation.

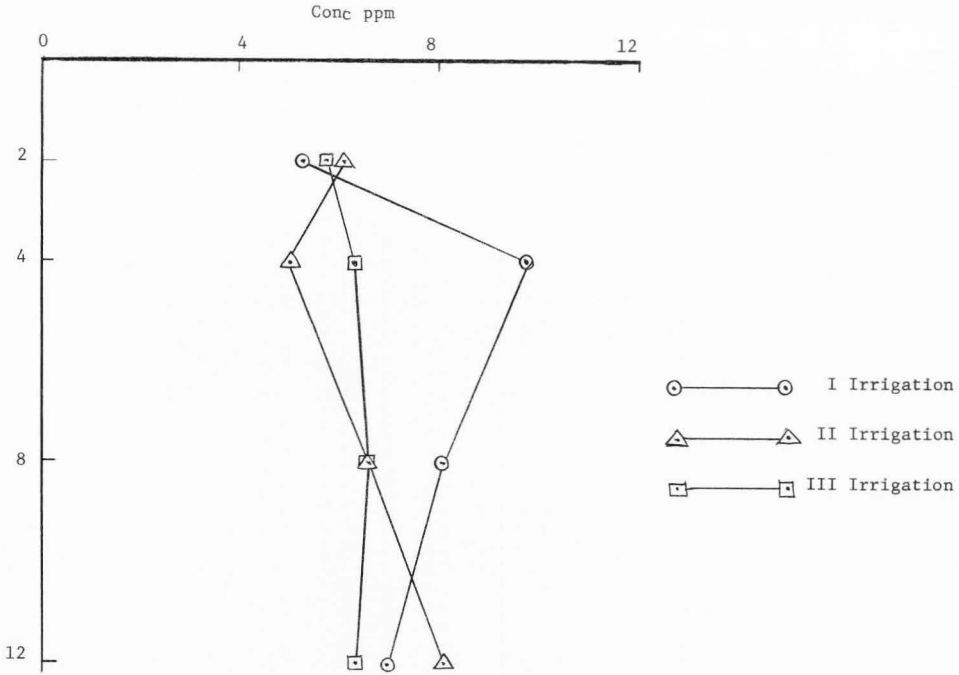


Figure 7. Quantity of atrazine in ppm found in soil solution at 4 soil depths at a distance of 5 inches from the furrow after each irrigation.

due to the downward movement of water under saturated conditions, just after stopping the irrigation.

At the time of second irrigation, the corn seedlings were nearly one month old and their root systems were able to take up herbicide in a considerable quantity. This seems to be the reason for a low and constant concentration of herbicide during the second and third irrigations.

Except at the center of the furrow, the water applied in the furrow did not have an opportunity to pass through the soil where the herbicide had been applied. The water could wet the soil only from under the surface or by lateral movement. Thus, the water could only act through diluting the concentration or by causing part of the herbicide to move downward by diffusion. Since all the herbicide was placed on the surface initially and all the water was placed in the furrow, there was probably little movement of herbicide directly downward at the 5-inch (12.7 cm) distance. Hence, all the herbicide at the intermediate and lower depths was carried there by water moving laterally from the furrow.

Drainage of water below the furrow probably accounts for the lack of accumulation of herbicide in the bottom layers of soil at the 0 and 2.5 inch (6.35 cm) distance.

## Overall Distribution

To get an idea of general distribution in the soil profile after each irrigation, the contour lines depicting concentrations of herbicide in ppm are plotted in the whole profile. The contour diagrams

for the first, second and third irrigation are plotted in figures 8, 9 and 10, respectively. From these contour diagrams it can be observed that the distribution of herbicide in soil profile is governed by the number of irrigations. Since the water is applied in the furrow the concentration contours show the probable accumulation of herbicide.

After the first irrigation, the concentration peak appears at a distance of 2.5 inches (6.35 cm) and a depth of 4 inches (10.2 cm) from the surface. There is a lower concentration under the furrow.

After the second and third irrigation, the concentration lines appear at lower depths under the furrow and shallow depth at some distances on either side of the furrow.

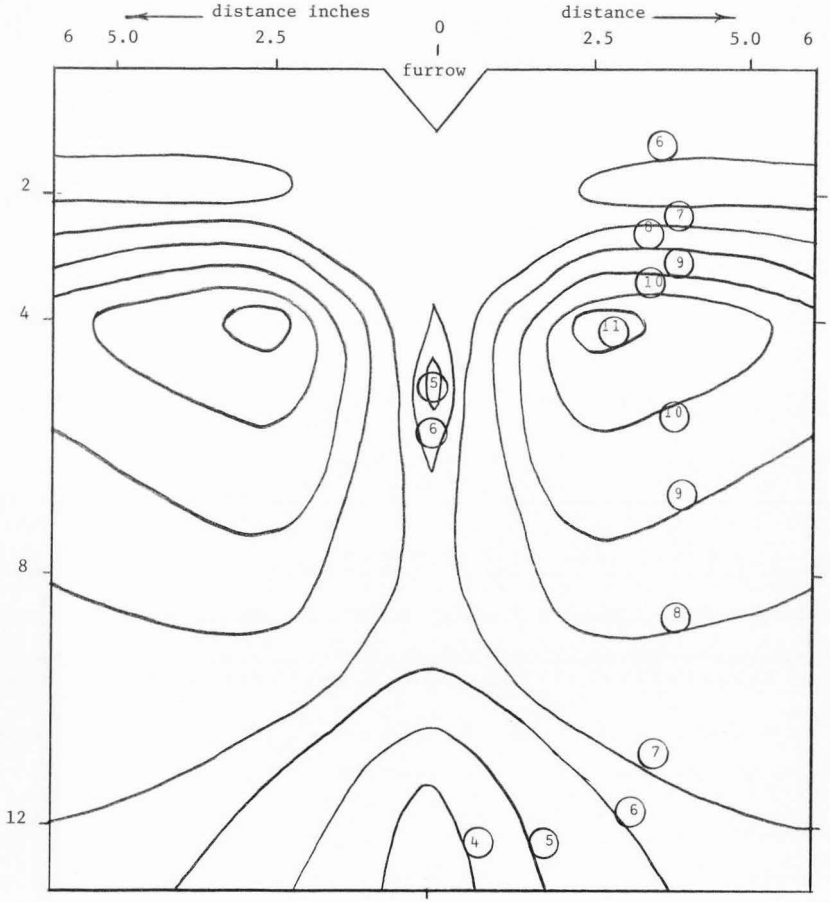


Figure 8. Distribution of atrazine in ppm in the soil profile after first irrigation.

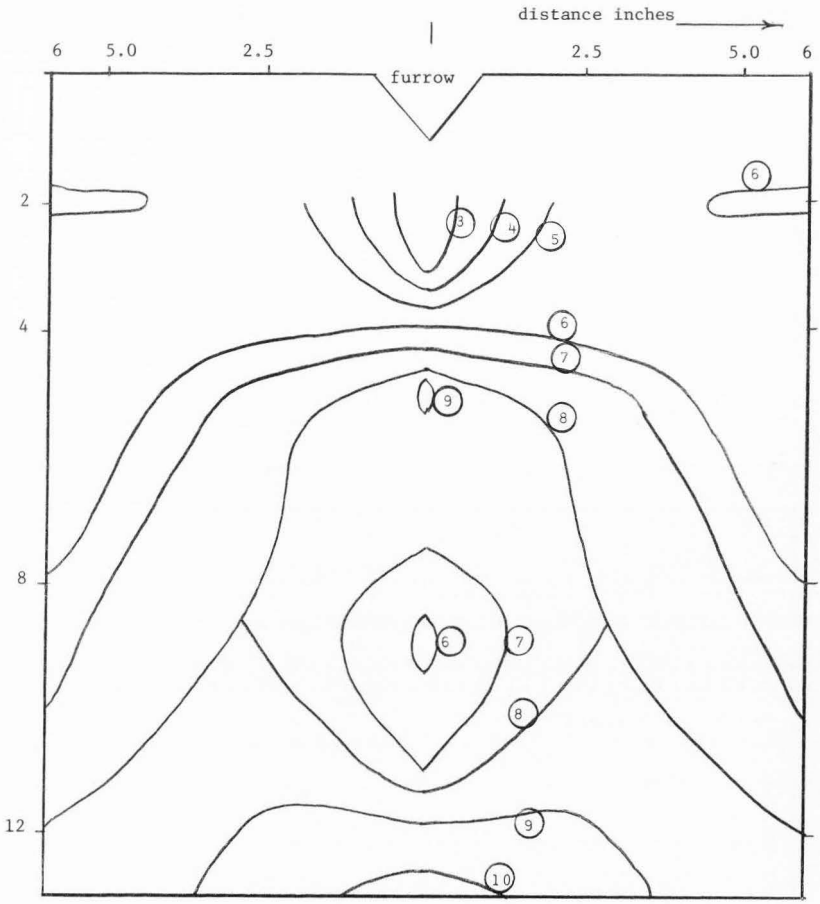


Figure 9. Distribution of atrazine in ppm in the soil profile after second irrigation.

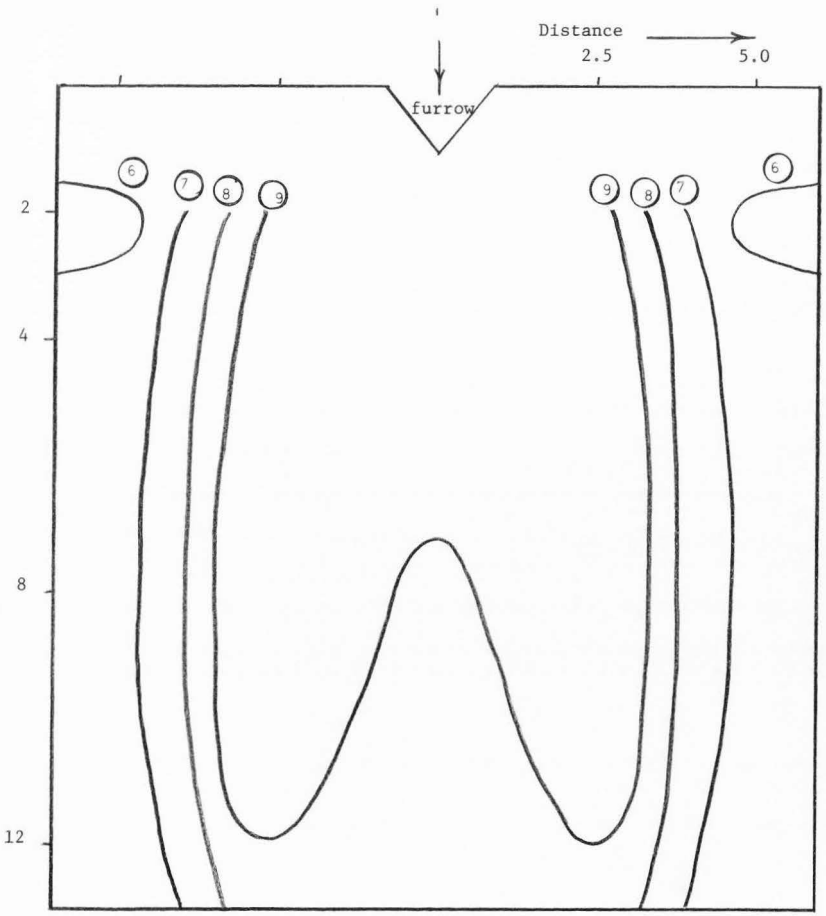


Figure 10. Distribution of atrazine in ppm in the soil profile after the third irrigation.

## SUMMARY AND CONCLUSION

Atrazine applied to the soil surface moved into the soil readily with irrigation water. Some herbicide moves with the wetting front. The pattern of movement apparently follows the chromatographic theory. The herbicide, once moved to a certain depth, redistributes in the soil profile due to mass movement of water and diffusion of the chemical. Since the corn takes the herbicide readily into the system, and converts it to harmless compounds, accumulation of herbicide in the soil is not of permanent nature.

It appears that atrazine is strongly adsorbed to the soil such that the amount in solution at any time is in local dynamic equilibrium with the adsorbed portion.

## SUGGESTIONS FOR FUTURE RESEARCH

(1) Studies on the movement of compounds on soil without the crops may yield information on the moving patterns so that interaction of plant uptake can be evaluated.

(2) Some methods to take samples from the soil profile before giving irrigations, need to be devised so that the redistribution of chemicals can be evaluated, since with the technique used it was not possible to take samples from the soil without disturbing the profile.

(3) Application of irreversible thermodynamic theory needs to be investigated further for describing the simultaneous movement of water and herbicides under field conditions.

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# APPENDIX

Table 10. Concentration of atrazine in parts per million in response to irrigations at different depths from the surface and distances from the center of the furrow.

| Irrigation | Distance inches | Distance cm | Depth inches | Depth cm | | | | |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 2 | 5.1 | 7.00 | 6.00 | 9.50 | 22.50 |
| | | | 4 | 10.2 | 3.75 | 4.25 | 4.50 | 12.50 |
| | | | 8 | 20.4 | 4.50 | 12.75 | 2.75 | 20.00 |
| | | | 12 | 30.0 | 2.50 | 6.75 | 0.50 | 9.75 |
| | 2.5 | 6.35 | 2 | 5.1 | 6.75 | 5.50 | 5.00 | 17.25 |
| | | | 4 | 10.2 | 8.25 | 13.00 | 13.25 | 34.50 |
| | | | 8 | 20.4 | 12.50 | 3.25 | 10.00 | 25.75 |
| | | | 12 | 30.0 | 7.00 | 5.50 | 5.75 | 18.25 |
| | 5 | 12.7 | 2 | 5.1 | 5.75 | 3.50 | 6.50 | 15.75 |
| | | | 4 | 10.2 | 8.75 | 10.75 | 9.75 | 29.25 |
| | | | 8 | 20.4 | 10.00 | 7.25 | 7.00 | 24.25 |
| | | | 12 | 30.0 | 8.25 | 6.75 | 6.00 | 21.00 |
| 2 | 0 | 0 | 2 | 5.1 | 2.00 | 3.50 | 1.25 | 6.75 |
| | | | 4 | 10.2 | 11.75 | 11.00 | 4.75 | 27.50 |
| | | | 8 | 20.4 | 4.00 | 4.25 | 8.75 | 17.00 |
| | | | 12 | 30.0 | 11.50 | 9.25 | 11.25 | 32.00 |
| | 2.5 | 6.35 | 2 | 5.1 | 6.25 | 5.50 | 5.75 | 17.50 |
| | | | 4 | 10.2 | 7.75 | 8.00 | 6.75 | 22.50 |
| | | | 8 | 20.4 | 8.00 | 8.25 | 7.75 | 24.00 |
| | | | 12 | 30.0 | 11.75 | 6.50 | 10.00 | 28.25 |
| | 5 | 12.70 | 2 | 5.1 | 8.75 | 4.50 | 5.00 | 18.25 |
| | | | 4 | 10.2 | 5.25 | 4.75 | 5.00 | 15.00 |
| | | | 8 | 20.4 | 6.25 | 5.75 | 7.75 | 19.75 |
| | | | 12 | 30.0 | 10.50 | 8.50 | 5.25 | 24.25 |
| 3 | 0 | 0 | 2 | 5.1 | 10.00 | 10.75 | 8.50 | 29.25 |
| | | | 4 | 10.2 | 9.00 | 9.75 | 9.00 | 27.75 |
| | | | 8 | 20.4 | 9.50 | 8.75 | 7.75 | 26.00 |
| | | | 12 | 30.0 | 8.75 | 9.25 | 9.00 | 27.00 |
| | 2.5 | 6.35 | 2 | 5.1 | 9.75 | 9.75 | 9.25 | 28.75 |
| | | | 4 | 10.2 | 10.50 | 9.50 | 8.50 | 28.50 |
| | | | 8 | 20.4 | 9.50 | 9.50 | 9.75 | 28.75 |
| | | | 12 | 30.0 | 9.00 | 9.75 | 8.00 | 26.75 |
| | 5 | 12.70 | 2 | 5.1 | 6.50 | 6.25 | 4.50 | 17.25 |
| | | | 4 | 10.2 | 6.00 | 6.25 | 6.75 | 19.00 |
| | | | 8 | 20.4 | 7.25 | 6.75 | 5.75 | 19.75 |
| | | | 12 | 30.0 | 5.25 | 6.25 | 7.50 | 19.00 |
| | | | | | 279.75 | 267.50 | 254.00 | 801.25 |